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(54) Preparing method of polycarbonate

(57) The present invention provides a method for manufacturing polycarbonate having outstanding color matching, outstanding retention of stability during molding, such as thermal stability and color-matching stability, and outstanding transparency and water resistance.

The method is characterized in that (a) a nitrogen-containing basic compound is used as a catalyst dissolved or dispersed in a monohydroxy compound or an aqueous solution of a monohydroxy compound. This catalyst solution is added to a melt polycondensation reaction system, and an aromatic dihydroxy compound and a carbonic acid diester are subjected to melt polycondensation. It is preferable to use a monohydroxy compound produced as a by-product of a polycondensation reaction between an aromatic dihydroxy compound and a carbonic acid diester as the monohydroxy compound, and it is particularly preferable that the aromatic monohydroxy compound is a phenol.

Description

The present invention relates to a method for manufacturing polycarbonate, and more specifically, to a method for manufacturing polycarbonate in which polycarbonate having outstanding color matching, outstanding thermal stability and color-matching stability during molding, and outstanding transparency and water resistance can be efficiently and easily manufactured

Polycarbonate has outstanding mechanical properties such as impact resistance, it is outstanding in thermal resistance, transparency, etc., and it is widely applied in products such as various machine components, optical discs, and automobile components.

This polycarbonate has conventionally been manufactured by the method of direct reaction of an aromatic dihydroxy compound such as bisphenol with phosgene (the surface method) or the method of an ester exchange reaction between an aromatic dihydroxy compound and a carbonic acid diester (the melt method).

Between these two methods, the melt method offers the advantage of allowing cheaper manufacturing of polycarbonate than the surface method. Moreover, the melt method is also preferred from the standpoint of environmental hygiene, as it does not use toxic substances such as phosgene

Moreover, in the melt method, the polycondensation reaction between the aromatic dihydroxy compound and the carbonic acid diester is carried out over a long period at a high temperature For this reason, the polycarbonate produced during the manufacturing process is subjected to high temperatures for long periods, causing polycarbonate to be obtained which shows yellow discoloration

Examples of inventions which have been proposed in order to solve these problems include the method for manufacturing polycarbonate of Japanese Laid-Open Patent Application No. 90-175723, in which a nitrogen-containing basic compound and a small amount of an alkali metal or alkaline earth metal were used in combination as a catalyst, and the method of Japanese Laid-Open Patent No. 93-9285, which involved the manufacture of polycarbonate using an even smaller amount of an alkali metal or alkaline earth metal as a catalyst. Moreover, Japanese Laid-Open Patent No 94-329786 presents a method for manufacturing polycarbonate in which an aromatic dihydroxy compound and diaryl carbonate are subjected to polycondensation in the presence of a solution or suspension composed of an alkali metal compound and/or alkaline earth metal compound and a catalyst having a boiling point of 30-250°C and having a dissolved oxygen concentration of 100 ppm or less.

When polycarbonate is manufactured by the melt method described above, in which small amounts of an alkali metal and/or alkaline earth metal catalyst are used as a catalyst, this allows polycarbonate to be obtained which has outstanding initial color-matching properties.

Moreover, this melt method can also be expected to provide a method for manufacturing polycarbonate having even more outstanding color-matching properties.

The purpose of the present invention is to provide a method for manufacturing polycarbonate in which an aromatic dihydroxy compound and a carbonic acid diester can be efficiently subjected to melt polycondensation using a small amount of a catalyst, allowing polycarbonate to be obtained which shows outstanding color-matching properties, has outstanding retention stability during molding such as thermal stability and color-matching stability, and shows outstanding water resistance.

The method for manufacturing polycarbonate of the present invention is characterized in that when an aromatic dihydroxy compound and a carbonic acid diester are subjected to melt polycondensation in the presence of a catalyst including (a) a nitrogen-containing basic compound.

the aforementioned (a) nitrogen-containing basic compound is dissolved or dispersed in a monohydroxy compound or an aqueous solution of a monohydroxy compound to make a catalyst solution, this catalyst solution is added to the melt polycondensation reaction system, and the aromatic dihydroxy compound and the carbonic acid diester are subjected to melt polycondensation.

As the method for manufacturing polycarbonate according to the present invention uses a solution or suspension of a monohydroxy compound in which a specified catalyst can be easily dissolved in the melt polycondensation system, this makes it possible to rapidly and uniformly disperse the catalyst in the reaction system and to carry out the melt polycondensation reaction in a stable manner from the initial stages of the reaction. Accordingly, this makes it possible to prevent the production of colorants as byproducts due to the presence of the catalyst in uneven amounts, thus allowing the manufacture of polycarbonate with outstanding color-matching properties.

In the present invention, it is preferable to use a monohydroxy compound produced as a by-product of a polycondensation reaction between an aromatic dihydroxy compound and a carbonic acid diester as the monohydroxy compound which forms the aforementioned catalyst solution, and it is particularly preferable if the aromatic monohydroxy compound is a phenol.

The aforementioned (a) nitrogen-containing basic compound may be used in the amount of 1×10^{-6} to 1×10^{-1} moles with respect to 1 mole of the aromatic dihydroxy compound.

Moreover, in the present invention, one may use (b) an alkali metal compound and/or alkaline earth metal com-

pound together with the aforementioned (a) nitrogen-containing basic compound as a polycondensation catalyst.

The following is a specific explanation of the method for manufacturing polycarbonate of the present invention.

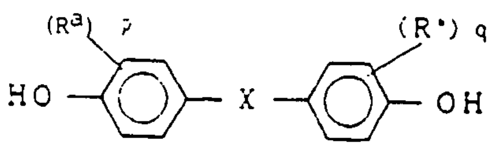
In the method for manufacturing polycarbonate of the present invention. polycarbonate is manufactured by subjecting an aromatic dihydroxy compound and a carbonic acid diester to melt polycondensation in the presence of a catalyst including (a) a nitrogen-containing basic compound.

In the present invention. the catalyst solution may be formed by dissolving or dispersing this (a) nitrogen-containing basic compound in the monohydroxy compound or by dissolving or dispersing it in an aqueous solution of the monohydroxy compound. the catalyst solution is then added to the melt polycondensation system. and the aromatic dihydroxy compound and the carbonic acid diester are subjected to melt polycondensation.

The various components and catalysts used in the present invention will first be explained.

Aromatic dihydroxy compounds

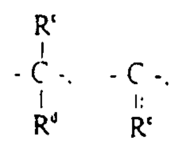
There are no particular restrictions on the aromatic dihydroxy compound used in the present invention. and an example is shown in Fig. [I] below.



... [I]

(In the formula. R^a and R^b are halogen atoms or monovalent hydrocarbon groups. and these may be identical or different. p and q are integers from 0-4

X is

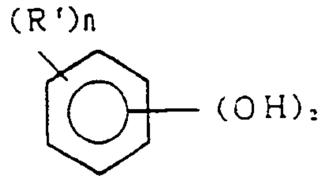


-O-. -S-. -SO-. or $-SO_2-$. R^c and R^d are hydrogen atoms or monovalent hydrocarbon groups. and R^e is a bivalent hydrocarbon group.)

Specific examples of the aromatic dihydroxy compound shown in Formula [I] include a bis(hydroxyaryl)alkane such as bis(4-hydroxyphenyl)methane.

1.1-bis(4-hydroxyphenyl)ethane.
2.2-bis(4-hydroxyphenyl)propane.
2.2-bis(4-hydroxyphenyl)butane.
2.2-bis(4-hydroxyphenyl)octane.
bis(4-hydroxyphenyl)phenylmethane.
2.2-bis(4-hydroxy-1-methylphenyl)propane.
1.1-bis(4-hydroxy-t-butylphenyl)propane.
or 2.2-bis(4-hydroxy-3-bromophenyl)propane
a bis(hydroxyaryl)cycloalkane such as 1.1-bis(4-hydroxyphenyl)cyclopentane or 1.1-(4-hydroxyphenyl)cyclohexane:
a dihydroxyaryl ether such as 4.4'-dihydroxydiphenyl ether or 4.4'-dihydroxy-3.3'-dimethyldiphenyl ether:
a dihydroxydiaryl sulfide such as 4.4'-dihydroxydiphenyl sulfide or 4.4'-dihydroxy-3.3'-dimethyldiphenyl sulfide:
a dihydroxydiaryl sulfoxide such as 4.4'-dihydroxydiphenyl sulfoxide or 4,4'-dihydroxy-3.3'-dimethyldiphenyl sulfoxide:
or a dihydroxydiaryl sulfone such as 4,4'-dihydroxydiphenyl sulfone or 4,4'-dihydroxy-3.3'-dimethyldiphenyl sulfone.

Among these compounds, the use of 2.2-bis(4-hydroxyphenyl)propane (bisphenol A) is particularly preferred. Moreover, the compound shown in Formula [II] below may also be used as the aromatic dihydroxy compound.



... [II]

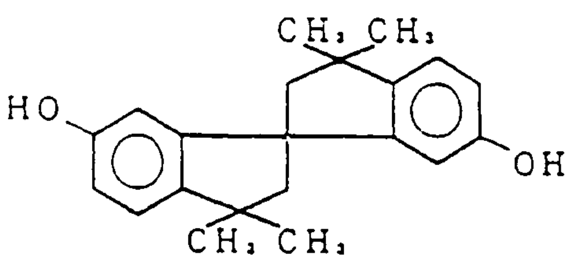
(Where R^f is a halogen atom or a hydrocarbon group or halogen-substituted hydrocarbon group having a 1-10 carbon atoms and n is an integer from 0 to 4 When n is 2 or above. R^f may be either identical or different.)

Specific examples of the aromatic dihydroxy compound shown in Formula [II] include resorcinol and substituted resorcinols such as 3-methylresorcinol 3-ethylresorcinol. 3-propylresorcinol. 3-butylresorcinol. 3-t-butylresorcinol. 3-phenylresorcinol. 3-cumylresorcinol 2.3.4.6-tetrafluororesorcinol. or 2.3.4.6-tetrabromoresorcinol:

catechol:

or a hydroquinone or a substituted hydroquinone such as 3-methylhydroquinone. 3-ethylhydroquinone. 3-propylhydroquinone. 3-butylhydroquinone. 3-t-butylhydroquinone. 3-phenylhydroquinone, 3-cumylhydroquinone. 2.3 5 6-tetramethylhydroquinone 2 3.5.6-tetra-t-butylhydroquinone. 2.3.5.6-tetrafluorohydroquinone. or 2 3.5.6-tetrabromohydroquinone

Moreover. in the present invention. the 2.2.2'.2'-tetrahydro-3.3.3'.3'-tetramethyl-1.1'-spirobis[IH-indene]-6.6'-diol shown in the following formula may also be used as the aromatic dihydroxy compound.



The aforementioned aromatic dihydroxy compound may also be a combination of 2 or more substances.

Moreover. specific examples of the carbonic acid diester include

diphenyl carbonate.
ditolyl carbonate.
bis(chlorophenyl) carbonate
m-cresyl carbonate.
dinaphthyl carbonate.
bis(diphenyl) carbonate.
diethyl carbonate.
dimethyl carbonate.
dibutyl carbonate.
and dicyclohexyl carbonate.

Of these substances. diphenyl carbonate should preferably be used.

These carbonic acid diesters may be used individually or in combination.

The carbonic acid diester used in the present invention should preferably contain a dicarboxylic acid or dicarboxylic acid ester. Specifically, the carbonic acid diester should preferably contain 50 mole % or less of dicarboxylic acid or dicarboxylic acid ester. with a content of 30 mole % or less being particularly preferable.

Examples of this dicarboxylic acid or dicarboxylic acid ester include

aromatic carboxylic acids such as terephthalic acid. isophthalic acid. diphenyl terephthalate, or diphenyl isophthalate:

aliphatic dicarboxylic acids such as succinic acid. glutaric acid, adipic acid. pimelic acid. suberic acid. azelaic acid, sebacic acid, decanedioic acid. dodecanedioic acid. diphenyl sebacate. diphenyl decanedioate. or diphenyl dodecanedioate:

and aliphatic dicarboxylic acids such as dichloropropanedicarboxylic acid. 1.2-cyclopropanedicarboxylic acid. 1.3-cyclobutanedicarboxylic acid. 1.2-cyclopentanedicarboxylic acid. 1.3-cyclopentanedicarboxylic acid. 1.2-cyclohexanedicarboxylic acid. 1.3-cyclohexanedicarboxylic acid. 1.4-cyclohexanedicarboxylic acid, diphenyl cyclopropanedicarboxylate. diphenyl 1.2-cyclobutanedicarboxylate, diphenyl 1,3-cyclobutanedicarboxylate. diphenyl 1.2-cyclopentanedicarboxylate. diphenyl 1.3-cyclopentanedicarboxylate. diphenyl 1,2-dicyclohexanedicarboxylate. diphenyl 1.3-cyclohexanedicarboxylate. or diphenyl 1.4-cyclohexanedicarboxylate.

The carbonic acid diester may contain 2 or more of these dicarboxylic acids or dicarboxylic acid esters.

In the present invention. in polycondensation of the carbonic acid diester and aromatic dihydroxy compound as described above. one should ordinarily use 1.0-1 30 moles of the carbonic acid diester for each mole of the aromatic dihydroxy compound. with an amount of 1 01-1.20 moles being particularly preferred.

Moreover. in manufacturing polycarbonate by the method of the present invention. together with the aforementioned aromatic dihydroxy compound and carbonic acid diester. a multifunctional compound having three or more functional groups per molecule may also be used.

A compound having a phenolic hydroxyl group or a carboxyl group should preferably be used as this multifunctional compound. with compounds containing three phenolic hydroxyl groups being particularly preferred. Specific examples of this multifunctional compound include

1.1.1-tris(4-hydroxyphenyl)ethane.
2.2'.2"-tris(4-hydroxyphenyl)triisopropylbenzene.
α-methyl-α.α' α'-tris(4-hydroxyphenyl)-1.4-diethylbenzene.
α.α'.α"-tris(4-hydroxyphenyl)-1.3.5-triisopropylbenzene.
phloroglucinol.
4.6-dimethyl-2.4-6-tris(4-hydroxyphenyl)heptane-2 [sic].
1.3.5-tris(4-hydroxyphenyl)benzene.
2.2-bis[4 4-(4 4'-dihydroxyphenyl)cyclohexyl]propane [sic].
trimellitic acid.
1.3.5-benzenetricarboxylic acid.
and pyromellitic acid

Of these compounds. the use of 1.1.1-tris(4-hydroxyphenyl)ethane or α.α'-α"-tris(4-hydroxyphenyl)-1.3.5-triisopropylbenzene. etc.. is particularly preferred.

This type of multifunctional compound should preferably be present in the amount of 0.03 moles or less with respect to 1 mole of the aromatic dihydroxy compound, and more preferably in the amount of 0.001-0.02 moles. with 0.001-0.01 moles being particularly preferred.

In manufacturing the polycarbonate. the aforementioned aromatic dihydroxy compound and the carbonic acid diester may be used in a solid state. or they may be subjected to the reaction in a molten state directly from the manufacturing device.

Catalysts

In the present invention. a catalyst including (a) a nitrogen-containing basic compound is used as the polycondensation catalyst.

For example. one may use a nitrogen-containing basic compound which decomposes readily or is volatile at high temperatures as this (a) nitrogen-containing basic compound. with specific examples including the following compounds:

Ammonium hydroxides having alkyl. aryl. and araryl groups. such as tetramethylammonium hydroxide (Me_4NOH). tetraethylammonium hydroxide (Et_4NOH), tetrabutylammonium hydroxide (Bu_4NOH). and trimethylbenzylammonium hydroxide (ϕ-$CH_2(Me)_3NOH$). etc.,
tertiary amines such as trimethylamine. triethylamine. dimethylbenzylamine. and triphenylamine,
secondary amines indicated by the formula R_2NH (in the formula. R indicates an alkyl group such as methyl or ethyl or an aryl group such as phenyl or tolyl),
primary amines indicated by the formula RNH_2 (in the formula. R has the same meaning as indicated above).
pyridines such as 4-dimethylaminopyridine. 4-diethylaminopyridine. and 4-pyrrolidinopyridine.
imidazoles such as 2-methylimidazole and 2-phenylimidazole.
or basic salts such as ammonia. tetramethylammonium borohydride (Me_4NBH_4). tetrabutylammonium borohydride (Bu_4NBH_4). tetrabutylammonium tetraphenylborate (Bu_4NBPh_4). and tetramethylammonium tetraphenylborate

(Me_4NBPh_4).

Of these substances, tetraalkylammonium hydroxides, particularly tetraalkylammonium hydroxides for electronic use which have a low content of metal impurities, are particularly preferable.

The aforementioned (a) nitrogen-containing basic compound should be included in the amount of 10^{-6} to 10^{-1} moles, or preferably 10^{-5} to 10^{-2} moles, with respect to 1 mole of the aromatic dihydroxy compound.

In the present invention, the catalyst is used in the form of a catalyst solution obtained by dissolving or dispersing the aforementioned (a) nitrogen-containing basic compound in a monohydroxy compound or aqueous solution of a monohydroxy compound.

Examples of this monohydroxy compound include aliphatic monohydroxy compounds (alcohols) and aromatic monohydroxy compounds (phenols), etc.

In the present invention, this monohydroxy compound should preferably be the same as the monohydroxy compound formed as a by-product of the polycondensation reaction between the aromatic dihydroxy compound and the carbonic acid diester. When it is the same as the monohydroxy compound formed as a by-product of a polycondensation reaction with the monohydroxy compound which forms the catalyst solution, compatibility between the catalyst solution and the mixed solution of the aromatic dihydroxy compound and the carbonic acid diester increases, making it possible to effectively disperse the catalyst ((a) the nitrogen-containing basic compound) in the reaction system and to simplify the process of recovery of unreacted monomers and monohydroxy compounds, etc.

Furthermore, the boiling point of the monohydroxy compound at constant pressure should preferably be equal to or greater than the temperature of the polycondensation reaction between the aromatic dihydroxy compound and the carbonic acid diester.

The monohydroxy compound formed as a by-product of the polycondensation reaction may be estimated based on the kind of carbonic acid diester used in the polycondensation reaction. Accordingly, the monohydroxy compound which forms the catalyst solution can be selected according to the carbonic acid diester used in the polycondensation reaction, and the following are specific examples of monohydroxy compounds which are used.

Carbonic acid diesters used in polycondensation reaction	Monohydroxy compounds produced as a by-product
Diphenyl carbonate	.. Phenol
Ditolyol carbonate	.. Cresol
Bis(chlorophenyl)carbonate	. Chlorophenol
Dinaphthyl carbonate	.. Naphthol
Bis(diphenyl)carbonate	.. Cumylphenol [sic]
Diethyl carbonate	.. Ethanol
Dimethyl carbonate	.. Methanol
Dibutyl carbonate	.. Butanol
Dicyclohexyl carbonate	.. Cyclohexanol

Of these substances, an aromatic monohydroxy compound is preferred, with a phenol being particularly preferred.

There are no particular restrictions on the amount of the aforementioned monohydroxy compound used with respect to (a) the nitrogen-containing basic compound, provided that this amount is not great enough to block the polycondensation reaction, but an amount of 0.5-10,000 moles with respect to 1 mole of (a) the nitrogen-containing basic compound is preferred, and an amount of 1-5,000 moles is particularly preferred.

Moreover, in the present invention, when the monohydroxy compound is water-soluble, it should preferably be used in the form of an aqueous solution of the monohydroxy compound for reasons of ease of operation.

There are no particular restrictions on the amount of water used in this case, provided that this amount does not block the polycondensation reaction, and there are also no particular restrictions on the ratio with respect to the monohydroxy compound, but an amount of 0.5-10,000 moles with respect to 1 mole of (a) the nitrogen-containing basic compound is preferred, with an amount of 1-5,000 moles being particularly preferable.

When (a) the nitrogen-containing basic compound is used in the form of a catalyst solution of a monohydroxy compound in this manner, the catalyst solution is rapidly dispersed in the polycondensation reaction system. Accordingly, compared to conventional methods in which a catalyst is directly added to the polycondensation reaction system of the aromatic dihydroxy compound and the carbonic acid diester or dissolved or dispersed in water or another solvent before being added, the occurrence of side reactions which cause discoloration is prevented from the initial stages of the melt polycondensation reaction, making it possible to obtain polycarbonate which has outstanding initial color tone immediately after polycondensation.

In the present invention, a combination of the aforementioned (a) nitrogen-containing basic compound and (b) an

alkali metal compound and/or alkaline earth metal compound (abbreviated below as (b) an alkali compound) may be used.

Specific examples of the preferred (b) alkali compound include organic acid salts, inorganic acid salts, oxides, hydroxides, hydrides, and alcoholates of alkali metals and alkaline earth metals.

More specifically, examples of the alkali metal compound include sodium hydroxide, potassium hydroxide, lithium hydroxide, sodium bicarbonate, potassium bicarbonate, lithium bicarbonate, sodium carbonate, potassium carbonate, lithium carbonate, sodium acetate, potassium acetate, lithium acetate, sodium stearate, potassium stearate, lithium stearate, sodium hydroxyborate, lithium hydroxycarborate, sodium phenyl borate, sodium benzoate, potassium benzoate, lithium benzoate, disodium hydrogen phosphate, dipotassium hydrogen phosphate, dilithium hydrogen phosphate, disodium salts, dipotassium salts, and dilithium salts of bisphenol A, and sodium salts, potassium salts, and lithium salts of phenol, etc.

Furthermore, specific examples of the alkaline earth metal compound include calcium hydroxide, barium hydroxide, magnesium hydroxide, strontium hydroxide, calcium bicarbonate, barium bicarbonate, magnesium bicarbonate, strontium bicarbonate, calcium carbonate, barium carbonate, magnesium carbonate, strontium carbonate, calcium acetate, barium acetate, magnesium acetate, strontium acetate, calcium stearate, barium stearate, magnesium stearate, strontium stearate, etc.

These substances may be used in combinations of 2 or more.

In the present invention, the (b) alkali compound should preferably be used in the amount of 5×10^{-8} to 2×10^{-6} moles for each mole of the aforementioned aromatic dihydroxy compound, or more preferably 1×10^{-7} to 1.5×10^{-6} moles, with the amount of 1×10^{-7} to 1.2×10^{-6} moles being particularly preferred. This value should preferably be the amount of the (b) alkali compound present in the polycondensation reaction system. Specifically, minute amounts of the (b) alkali compound are present in the raw materials as impurities, and in such cases, the total amount of the (b) alkali compound added as a catalyst and the (b) alkali compound present in the raw materials as an impurity should preferably be the amount specified above.

However, as the amount of the (b) alkali compound present in the raw materials as an impurity varies depending on the raw material used, in order to accurately control the amount of the (b) alkali compound present in the reaction system, it is preferred to purify the raw materials used in order to minimize the amount of the (b) alkali compound present in the raw material. For example, the raw material should preferably be purified and used in the reaction in such a manner that the amount of the (b) alkali compound present in the various components of the raw material is 1 ppb or less as calculated by metal conversion.

In the present invention, it is preferable to use a combination of the aforementioned basic catalysts, (a) the nitrogen-containing basic compound and (b) the alkali compound, as the polycondensation catalyst.

When (a) the nitrogen-containing basic compound and (b) the alkali compound are used in the aforementioned amounts as a catalyst, it becomes possible to carry out the polycondensation reaction at a sufficient rate and to produce high-molecular-weight polycarbonate having a high degree of polymerization.

Moreover, in the present invention, a combination of the above-mentioned basic catalysts and (c) a boric acid compound may also be used as the polycondensation catalyst.

Examples of this type of (c) boric acid compound include boric acid and boric acid esters.

As an example of a boric acid ester, one can mention a boric acid ester having the following general formula.

$$B(OR)_n(OH)_{3-n}$$

In the formula, R indicates an alkyl group such as methyl or ethyl or an aryl group such as phenyl, and n is the integer 1, 2, or 3.

Specific examples of this boric acid ester include trimethyl borate, triethyl borate, tributyl borate, trihexyl borate, triheptyl borate, triphenyl borate, tritolyl borate, and trinaphthyl borate.

The (c) boric acid or boric acid ester used as a catalyst in the present invention should be used in the amount of 10^{-8} to 10^{-1} moles, and preferably 10^{-7} to 10^{-2} moles, with respect to 1 mole of the aromatic dihydroxy compound, with the amount of 10^{-6} to 10^{-4} moles being particularly preferred.

Moreover, the following acidic catalysts may be used in the present invention.

Examples of these acidic catalysts include Lewis acid compounds such as the following:

zinc compounds such as zinc borate, zinc acetate, zinc oxalate, zinc phenylacetate, zinc chloride, zinc sulfate, zinc nitrate, zinc carbonate, zinc oxide, zinc hydroxide, zinc stearate, zinc-chromium oxide, and zinc-chromium-copper oxide,
cadmium compounds such as cadmium acetate, cadmium oxalate, cadmium oxide, and cadmium stearate,
silicon compounds such as silicon oxide, silica alumina, and silica magnesia,
germanium compounds such as germanium oxide and germanium hydroxide,
tin compounds such as stannous acetate, stannous oxalate, tin octylate, stannous chloride, stannic chloride, stan-

nous oxide. stannic oxide. and tetraphenyltin.

lead compounds such as lead acetate. lead borate. lead citrate. lead hydroxide. lead oxide. lead phosphates. lead phthalate. and lead stearate.

antimony compounds such as antimony acetate. antimony oxalate. triphenylantimony. antimony trioxide. antimony pentaoxide. triphenoxyantimony. trimethoxyantimony. and antimony trichloride.

bismuth compounds such as bismuth acetate. bismuth oxalate. triphenylbismuth. bismuth trioxide. and bismuth trichloride.

and titanium compounds such as titanium trichloride. titanium tetrachloride. titanium dioxide. tetraphenoxytitanium, and tetraisopropoxytitanium.

In the present invention. the (a) nitrogen-containing basic compound used in the above-mentioned polycondensation reaction is used in the form of a catalyst solution of a monohydroxy compound or monohydroxy compound aqueous solution. In cases where the other compounds mentioned above are used together with (a) the nitrogen-containing basic compound as the polycondensation catalyst. it is sufficient if at least the (a) nitrogen-containing basic compound is used as the catalyst solution of the monohydroxy compound or monohydroxy compound aqueous solution. For example. when (a) a nitrogen-containing basic compound and (b) an alkali compound are used in combination as the catalyst. the (a) nitrogen-containing basic compound alone may be dissolved or dispersed in the monohydroxy compound or monohydroxy compound aqueous solution. and (b) the alkali compound may be added directly or in the form of an aqueous solution. Moreover. one may also mix (a) and (b) in advance and then dissolve or disperse them in the monohydroxy compound or monohydroxy compound aqueous solution. and (a) and (b) may be separately dissolved or dispersed in the monohydroxy compound or monohydroxy compound aqueous solution and used individually, or separately dissolved or dispersed catalyst solutions may be mixed and then used.

In the present invention. the aromatic dihydroxy compound and the carbonic acid diester are subjected to melt polycondensation in the presence of a catalyst as described above.

In the presence of this catalyst. the melt polycondensation reaction between the aromatic dihydroxy compound and the carbonic acid diester may be carried out under conditions identical to those conventionally known for polycondensation reactions.

Specifically. the first stage reaction of the aromatic dihydroxy compound and the carbonic acid diester should be carried out at a temperature of 80-250°C. and preferably 100-230°C. with a temperature of 120-190°C being particularly preferable. It should be carried out for a period of 0-5 hours. and preferably 0-4 hours. with a period of 1-3 hours being particularly preferred. and should be carried out at constant pressure. Next. keeping the reaction system at reduced pressure. the reaction temperature is increased and the reaction between the aromatic dihydroxy compound and the carbonic acid diester is carried out. Finally. the polycondensation reaction between the aromatic hydroxy compound and the carbonic acid diester should preferably be carried out at a pressure of 5 mmHg or less. preferably 1 mmHg, and a temperature of 240-320°C.

In the process of the polycondensation reaction described above. the monohydroxy compound used as a catalyst solution is removed from the reaction system together with reaction byproducts.

In the present invention. the catalyst solution may be added at any stage of the polycondensation reaction.

The aforementioned polycondensation reaction may be carried out either continuously or by the batch method. Moreover. the reaction device used in conducting the aforementioned reaction may be of the tank. tube. or tower type.

The intrinsic viscosity of the polycarbonate obtained as a by-product as described above is ordinarily 0.10-1.0 dl/g as measured in methylene chloride at 20°C. with viscosity of 0.30-0.65 dl/g being preferred.

The manufacturing method of the present invention is desirable from the standpoint of environmental hygiene. as toxic substances such as phosgene and methylene chloride are not used in melt polycondensation.

The polycarbonate obtained as a reaction by-product as described above (referred to in the following as polycarbonate [A]) shows outstanding initial color matching.

In the above-described method for manufacturing polycarbonate of the present invention. when a basic catalyst, particularly (b) an alkali compound. is used as a catalyst. after melt polycondensation. when the [A] polycarbonate produced as a by-product is in a molten state. it is preferable to add [B] a sulfur-containing acidic compound having a pKa value of 3 or below and/or a derivative formed from said acidic compound (referred to hereinafter as [B] the acidic compound).

Moreover. [B] the acidic compound should preferably be added together with [C] water.

In the present invention. examples of [B] the sulfur-containing acidic compound or the derivative formed from said acidic compound include sulfurous acid. sulfuric acid. sulfinic acid-class compounds. sulfonic acid compounds, and their derivatives.

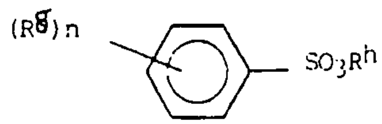
Specific examples of sulfurous acid derivatives include dimethyl sulfite, diethyl sulfite. dipropyl sulfite. dibutyl sulfite. and diphenyl sulfite.

Specific examples of sulfuric acid derivatives include dimethyl sulfate, diethyl sulfate, dipropyl sulfate. dibutyl sul-

fate. and diphenyl sulfate.

Examples of sulfinic acid-class compounds include benzenesulfinic acid. toluenesulfinic acid. and naphthalenesulfinic acid.

Moreover. an example of the sulfonic acid-class compound or its derivative is the compound shown in General Formula [III] below or an ammonium salt thereof.



... [III]

In the formula. R^g is a hydrocarbon group or halogen-substituted hydrocarbon group having 1-50 carbon atoms. R^h is a hydrogen atom or a hydrocarbon group or halogen-substituted hydrocarbon group having 1-50 carbon atoms. and n is an integer from 0-3.

Examples of this sulfonic acid-class compound or derivative thereof include:

sulfonates such as benzenesulfonate and p-toluenesulfonate,
sulfonic acid esters such as methyl p-toluenesulfonate. ethyl p-toluenesulfonate. butyl p-toluenesulfonate. octyl p-toluenesulfonate. and phenyl p-toluenesulfonate.
and sulfonic acid ammonium salts such as ammonium p-toluenesulfonate.

Moreover. sulfonic acid compounds such as trifluoromethanesulfonic acid. naphthalenesulfonic acid. sulfonated polystyrene. and methyl acrylate-sulfonated styrene copolymer may also be used.

These substances may also be used in combinations of two or more.

In the present invention. one should preferably use the sulfonic acid-class compound shown in General Formula [III] above or a derivative thereof as [B] the acidic compound.

In particular. one should preferably use an ester compound in which. in General Formula [III] above. R^g indicates a substituted aliphatic hydrocarbon group having 1-6 carbon atoms. R^h indicates a substituted aliphatic hydrocarbon group having 1-8 carbon atoms. and n indicates an integer from 0-3. Specific preferred examples include ethyl benzenesulfonate butyl benzenesulfonate, methyl p-toluenesulfonate, ethyl p-toluenesulfonate, and butyl p-toluenesulfonate.

Among these substances. methyl p-toluenesulfonate. ethyl p-toluenesulfonate. and butyl p-toluenesulfonate are particularly preferred.

These acidic compounds [B] may be used in combinations of two or more. In the present invention, the aforementioned [B] acidic compound should be used in an amount greater by a molar factor of 1-20 than the amount of the (b) alkali compound used in the reaction of the aforementioned [A] polycarbonate. and preferably greater by a molar factor of 1-10. with a molar factor of 1-8 being particularly preferred.

By adding the acidic compound [B] to the reaction product (polycarbonate [A]) in the above amounts, the alkali metal compound remaining in the polycarbonate is neutralized or weakened. making it possible to obtain polycarbonate in which final retention stability and water resistance are further improved.

Moreover, in the present invention. it is preferable to add the aforementioned [B] acidic compound together with [C] water in the amount of 5-1.000 ppm with respect to the polycarbonate [A]. or preferably 10-500 ppm. with the amount of 20-300 ppm being particularly preferred.

When [C] water is added together with [B] the acidic compound to [A] the polycarbonate manufactured using (b) an alkali compound in this manner. the neutralization efficacy of the [B] acidic compound which acts as a basic catalyst in [A] the polycarbonate is increased. making it possible to obtain polycarbonate which shows outstanding retention stability during melting and also has outstanding color matching, transparency, water resistance, and weather resistance properties.

Moreover. when more than 1.000 ppm of water is added. the polycarbonate becomes susceptible to hydrolysis. causing deterioration of the physical properties of the polycarbonate. In the present invention. the polycarbonate should preferably be obtained by adding the aforementioned [B] acidic compound and a small amount of [C] water to the [A] polycarbonate which is the reaction product and then kneading the mixture.

Kneading of the [A] polycarbonate. the [B] acidic compound. and [C] the water can be carried out using an ordinary kneading device such as a monoaxial extruder. a biaxial extruder. or a static mixer, and these mixing devices may be effectively used whether or not they are equipped with vents.

Specifically. the [B] acidic compound and [C] water should preferably be added while the [A] polycarbonate obtained by polycondensation is in the reactor or extruder in a molten state. The [B] acidic compound and [C] water may be added either separately or at the same time. and there are no restrictions on the order in which they are added, but

simultaneous addition is preferred.

More specifically, in manufacturing polycarbonate from [A] polycarbonate, [B] an acidic compound, and [C] water, for example, after forming the polycarbonate by adding [B] the acidic compound and [C] water to the [A] polycarbonate obtained from the polycondensation reaction in the reactor, one may pelletize the polycarbonate using an extruder, and while the [A] polycarbonate obtained from the polycondensation reaction is passing from the reactor through the extruder and being pelletized, one may add [B] the acidic compound and [C] water and knead this mixture to obtain the polycarbonate.

Generally speaking, in using polycarbonate, polycarbonate pellets are remelted and various additives such as thermal stabilizers are blended in. In the polycarbonate pellets obtained in the present invention, when the various additives are blended in, or even when melting is carded out during molding, as thermal stability is improved and retention stability during melting is outstanding, thermal decomposition due to melting in particular is inhibited, making the material resistant to decreases in molecular weight and discoloration.

Moreover, in the present invention, [D] an additive may also be added to the polycarbonate [A], provided this does not have an adverse effect on the purpose of the invention.

This [D] additive should preferably be added to the [A] polycarbonate which is in a molten state at the same time as [B] the acidic compound and [C] the water.

The [B] acidic compound and [C] water may be added to the polycarbonate [A] at the same time as [D] the additive, or the various components may be added separately. Moreover, among the [D] additives presented below, reactive additives should preferably be added after adding [B] the acidic compound and [C] water.

Generally speaking, a wide range of additives may be used in the present invention as additive [D] according to the desired purpose of use, with examples including thermal stabilizers, epoxy compounds, ultraviolet absorbers, mold-releasing agents, colorants, antistatic agents, slipping agents, antiblocking agents, lubricants, defogging agents, natural oils, synthetic oils, wax, organic fillers, and inorganic fillers.

Of these substances, one should preferably use substances such as the thermal stabilizers, epoxy compounds, ultraviolet light absorbers, mold-releasing agents, and colorants presented below. These substances may also be used in combinations of two or more.

Specific examples of the thermal stabilizer used in the present invention include phosphorus compounds, phenol-class stabilizers, organic thioether-class stabilizers, and hindered amine stabilizers.

Examples of the phosphorus compound which may be used include phosphoric acid, phosphorous acid, hypophosphorous acid, pyrophosphoric acid, polyphosphoric acid, phosphoric esters, and phosphorous esters.

Examples of these phosphoric esters include

trialkyl phosphates such as trimethyl phosphate triethyl phosphate, tributyl phosphate, trioctyl phosphate, tridecyl phosphate, trioctadecyl phosphate, distearylpentaerythrityl diphosphate, tris(2-chloroethyl) phosphate, and tris (2,3-dichloropropyl) phosphate,
tricycloalkyl phosphates such as tricyclohexyl phosphate,
and triaryl phosphates such as triphenyl phosphate, tricresyl phosphate, tris(nonylphenyl) phosphate, and 2-ethylphenyl diphenyl phosphate.

Moreover, an example of the phosphorous ester is a compound having the following general formula.

$$P(OR)_3$$

(Where R indicates an alicyclic hydrocarbon group, an aliphatic hydrocarbon group, or an aromatic hydrocarbon group. These may be either identical or different.)

Examples of the compound indicated by this formula include:

trialkyl phosphites such as trimethyl phosphite, triethyl phosphite, tributyl phosphite, trioctyl phosphite, tris(2-ethylhexyl) phosphite, trinonyl phosphite, tridecyl 1 phosphite, trioctadecyl phosphite, tristearyl phosphite, tris(2-chloroethyl) phosphite, and tris(2,3-dichloropropyl) phosphite,
tricycloalkyl phosphites such as tricyclohexyl phosphite,
triaryl phosphites such as triphenyl phosphite, tricresyl phosphite, tris(ethylphenyl) phosphite, tris(2,4-di-t-butylphenyl) phosphite, tris(nonylphenyl) phosphite, and tris(hydroxyphenyl) phosphite,
and aryl alkyl phosphites such as phenyl didecyl phosphite,

diphenyl decyl phosphite, diphenyl isooctyl phosphite, phenyl isooctyl phosphite, and 2-ethylhexyl diphenyl phosphite.

Moreover, examples of the phosphorous ester include distearyl pentaerythrityl diphosphite and bis(2,4-di-t-butylphenyl) pentaerythrityl diphosphite.

These compounds may also be used in combinations of 2 or more.

Among these substances. a phosphorous ester having the above-mentioned formula is preferred for use. with aromatic phosphorous ester being preferred. and tris(2.4-di-t-butylphenyl) phosphite being particularly preferred.

Examples of phenolic stabilizers include n-octadecyl 3-(4-hydroxy -3'.5'-di-t-butylphenyl)propionate. tetrakis[methylene-3-(3'.5'-di-t-butyl-4--hydroxyphenyl)propionate]methane [sic]. 1.1.3-tris(2-ethyl-4-hydroxy .-5-t-butylphenyl)butane. distearyl (4-hydroxy-3-methyl-5-t-butyl)benzylmalonate. and 4-hydroxymethyl-2.6-di-t-butylphenol.

Examples of thioether stabilizers include dilauryl thiodipropionate. distearyl thiodipropionate. dimyristyl 3.3'-thiodipropionate. ditridecyl 3.3'-thiodipropionate. and pentaerythritol tetrakis(beta-laurylthiopropionate).

Examples of the hindered amine stabilizer include bis(2.2.6.6-tetramethyl-4-piperidyl) sebacate. bis(1.2.2.6.6-pentamethyl-4-piperidyl) sebacate.1-[2-{3-(3.5-di-t-butyl-4-hydroxyphenyl)propionyloxy}ethyl]-4-{3-(3.5-di-t-butyl-4-hydroxyphenyl)propionyloxy}-2.2.6.6-tetramethylpiperidyl [sic]. 8-benzyl-7.7.9.9-tetramethyl-3-octyl-1.2.3-triazaspiro [4.5]undecane-2.4-dione.4-benzoyloxy-2.2.6.6-tetramethylpiperazine. 2-(3.5-di-t-butyl-4-hydroxybenzyl)-2-n-butyl malonate bis(1.2.2.6.6-pentamethyl-4-piperidyl) [sic]. and tetrakis(2.2.6.6-tetramethyl-4-piperadyl)1.2.3.4-butanetetracarboxylate.

These compounds may also be used in combinations of 2 or more.

These thermal resistance stabilizers should be used in an amount of 0.001-5 parts by weight with respect to 100 parts by weight of polycarbonate. and preferably 0.005-0.5 parts by weight. with an amount of 0.01-0.3 parts by weight being particularly preferred.

Moreover. the thermal resistance stabilizer may be added in either solid or liquid form.

This thermal stabilizer should preferably be added to [A] the polycarbonate together with [B] and [C] while the polycarbonate is in a molten state. as this makes it possible to manufacture a polycarbonate which has been heated only a few times during manufacturing. and as the polycarbonate pellets obtained contain a thermal stabilizer. one can inhibit thermal decomposition during remelting.

Moreover. as an epoxy compound. a compound is used which has one or more epoxy groups per molecule. Specific examples include the following:

epoxidized soy bean oil. epoxidized linseed oil. phenyl glycidyl ether. allyl glycidyl ether. t-butylphenyl glycidyl ether. 3.4-epoxycyclohexylmethyl 3'.4'-epoxycyclohexanecarboxylate. 3.4-epoxy-6-methylcyclohexylmethyl 3'.4'-epoxy-6'-methylcyclohexylcarboxylate. 2.3-epoxycyclohexylmethyl 3'.4'-epoxycyclohexanecarboxylate. 4-(3.4-epoxy-5-methylcyclohexyl)butyl 3'.4'-epoxycyclohexanecarboxylate. 3.4-epoxycyclohexylethylene oxide. cyclohexylmethyl 3.4-epoxycyclohexanecarboxylate. 3.4-epoxy-6-methylcyclohexylmethyl 6'-methylcyclohexanecarboxylate. bisphenol A diglycidyl ether. tetrabromobisphenol A glycidyl ether. diglycidyl ester of phthalic acid. diglycidyl esters of hexahydrophthalic acid. bis-epoxydicyclopentadienyl ether. bis-epoxyethylene glycol. bis-epoxycyclohexyl adipate. butadiene diepoxide. tetraphenylethylene epoxide. octyl epoxyphthalate. epoxidized polybutadiene. 3.4-dimethyl-1.2-epoxycyclohexane.3.5-dimethyl-1.2-epoxycyclohexane. 3-methyl-5-t-butyl-1.2-epoxycyclohexane. octaecyl 2.2-dimethyl-3.4-epoxycyclohexanecarboxylate. n-butyl 2.2-dimethyl-3.4-epoxycyclohexanecarboxylate. cyclohexyl 2-methyl-3.4-epoxycyclohexanecarboxylate. n-butyl 2-isopropyl-3.4-epoxy-5-methylcyclohexanecarboxylate. octadecyl 3.4-epoxycyclohexanecarboxylate. 2-ethylhexyl 3'.4'-epoxycyclohexylcarboxylate. 4.6-dimethyl-2.3-epoxycyclohexyl 3'.4'-epoxycyclohexanecarboxylate. 4.5-epoxytetrahydrophthalic anhydride. 3-t-butyl-4.5-epoxytetrahydrophthalic anhydride. diethyl 4.5-epoxy-cis-1.2-cyclohexanedicarboxylate. and di-n-butyl 3-t-butyl-4.5-epoxy-cis-1.2-cyclohexanedicarboxylate.

Of the above substances. an alicyclic epoxy compound should preferably be used. with 3.4-epoxycyclohexylmethyl 3'.4'-epoxycyclohexanecarboxylate being particularly preferred.

These substances may be also used in combinations of 2 or more.

This type of epoxy compound should be added in the amount of 1-2.000 ppm. and preferably 10-1.000 ppm. with respect to the aforementioned [A] polycarbonate..

In particular. when an epoxy compound is used as [D] the additive. one should preferably add the epoxy compound after adding [B] the acidic compound and [C] water in order to neutralize the excess [B] acidic compound. When this [B] acidic compound. which has been added in an excess amount. is neutralized with an epoxy compound. one can obtain polycarbonate which is particularly outstanding in water resistance and transparency.

There are no particular restrictions on the ultraviolet absorber used in the present invention. with an ordinary ultraviolet absorber being suitable. such as a salicylic acid ultraviolet absorber. a benzophenone ultraviolet absorber. a benzotriazole ultraviolet absorber. or a cyanoacrylate ultraviolet absorber.

Specific examples of salicylic acid ultraviolet absorbers include phenyl salicylate and p-t-butylphenyl salicylate.

Examples of benzophenone ultraviolet absorbers include 2.4-dihydroxybenzophenone. 2-hydroxy-4-methoxybenzophenone. 2.2'-dihydroxy-4-methoxybenzophenone. 2.2'-dihydroxy-4.4'-dimethoxybenzophenone. 2-hydroxy-4-methoxy-2'-carboxybenzophenone. 2-hydroxy-4-methoxy-5-sulfobenzophenone trihydrate. 2-hydroxy-4-n-octyloxybenzophenone. 2.2'.4.4'-tetrahydroxybenzophenone; 4-dodecyloxy-2-hydroxybenzophenone. bis(5-benzoyl-4-hydroxy-2-methoxyphenyl)methane. and 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid.

Examples of benzotriazole ultraviolet absorbers include 2-(2'-hydroxy-5'-methylphenyl)benzotriazole. 2-(2'-hy-

droxy-3'5-di-t-butylphenyl)benzotriazole. 2-(2'-hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole. 2-(2'-hydroxy-3' 5'-di-t-butylphenyl)-5-chlorobenzotriazole. 2-(2'-hydroxy-5'-t-octylphenyl)benzotriazole. 2-(2'-hydroxy-3',5'-di-t-amylphenyl)benzotriazole, 2-[2'-hydroxy-3'-(3".4".5".6"-tetrahydrophthalimidomethyl)-5'-methylphenyl] benzotriazole. and 2.2'-methylenebis[4-(1.1.3.3-tetramethylbutyl)-6-(2H-benzotriazol-2-yl)phenol].

Examples of cyanoacrylate ultraviolet absorbers include 2-ethylhexyl 2-cyano-3.3-diphenylacrylate and ethyl 2-cyano-3.3-diphenylacrylate. These substances may also be used in combinations of two or more.

Ultraviolet absorbers are ordinarily used in the amount of 0.001-5 parts by weight with respect to 100 parts by weight of [A] the polycarbonate. and preferably 0.005-10 parts by weight. with the amount of 0 01-0.5 parts by weight being particularly preferred.

Moreover. there are no particular restrictions on mold-releasing agents. with a generally-known mold-releasing agent being suitable.

For example. one may use hydrocarbon mold-releasing agents. including natural and synthetic paraffins. polyethylene waxes. and fluorocarbons.

fatty acid mold-releasing agents. including higher fatty acids such as stearic acid and hydroxystearic acid and oxy fatty acids.

fatty acid amine mold-releasing agents. including fatty acid amides such as stearic acid amide and ethylene bis-stearamide and alkylene bis-fatty acid amide.

alcohol mold-releasing agents. including aliphatic alcohols such as stearyl alcohol and cetyl alcohol, polyvalent alcohols. polyglycol. and polyglycerol.

fatty acid ester mold-releasing agents. including fatty acid lower alcohol esters such as butyl stearate and pentaerythritol tetrastearate. fatty acid polyvalent alcohol esters. and fatty acid polyglycol esters.

or silicone mold-releasing agents. including silicone oil. and these substances may be used in combinations of two or more

In the present invention. the mold-releasing agent should ordinarily be used in the amount of 0 001-5 parts by weight. and preferably 0.005-1 parts by weight. with respect to 100 parts by weight of the polycarbonate [A], with an amount of 0.01-0.5 parts by weight being particularly preferred.

The colorant used may be a pigment or a dye. Colorants include inorganic and organic colorants. and either may be used. or a combination of the two may be used.

Specific examples of inorganic colorants include oxides such as titanium dioxide and red iron oxide. hydroxides such as aluminum white. sulfides such as zinc sulfide. selenium. ferrocyanides such as Prussian blue. chromates such as zinc chromate and molybdenum red. sulfates such as barium sulfate. carbonates such as calcium carbonate. silicates such as ultramarine. phosphates such as manganese violet. carbons such as carbon black. and metal powder colorants such as bronze powder and aluminum powder.

Specific examples of organic colorants include nitroso colorants such as naphthol green B. nitro colorants such as naphthol yellow S. azo colorants such as lithol red. Bordeaux 10B. naphthol red. and chromophthal yellow. phthalocyanine colorants such as phthalocyanine blue and fast sky blue. and condensation polycyclic colorants such as indanthrone blue. quinacridone violet. and dioxazine violet.

These colorants are ordinarily used in the amount of 1×10^{-6} to 5 parts by weight with respect to 100 parts by weight of [A] the polycarbonate. and preferably 1×10^{-5} to 3 parts by weight. with the amount of 1×10^{-5} to 1 part by weight being particularly preferred.

Moreover. in the present invention. the above-mentioned [B] acidic compound. [C] water. and [D] additives are added to the polycarbonate [A] in a molten state as described above. but provided that the purpose of the invention is not impaired. these substances [B], [C]. and [D] may also be diluted with polycarbonate powder and added to the polycarbonate [A]. or one may add master pellets to the polycarbonate [A] which already contain high concentrations of [B], [C]. and [D]. In this case. as the water absorbed by the polycarbonate powder or pellets is included. this amount of absorbed water may be subtracted from the above-mentioned [C] water before it is added.

The above method for manufacturing polycarbonate of the present invention makes it possible to efficiently carry out a melt polycondensation reaction in which an aromatic dihydroxy compound and a carbonic acid diester are subjected to a melt polycondensation reaction using a specified catalyst. Accordingly, this makes it possible to efficiently manufacture polycarbonate which shows outstanding initial color-matching properties, has outstanding retention stability during molding such as thermal stability and color-matching stability, and shows outstanding transparency and water resistance.

Moreover, when additives such as acidic compounds are added as necessary to the reaction product when it is in a molten state immediately following the melt polycondensation reaction. the catalyst is stabilized, making it possible to obtain polycarbonate having improved thermal resistance, etc.

Polycarbonate manufactured by the method of the present invention can be favorably used not only in general

molded materials. but in construction materials such as sheets. automobile headlight lenses, optical lenses such as glasses. and optical recording media.

Practical Examples

The following is an explanation of the present invention with reference to practical examples, but the invention is not limited to these examples.

In the present specification, the intrinsic viscosity (IV), MFR, color matching [YI], optical transmittance, haze, retention stability, and water resistance of the polycarbonate were measured in the following manner.

Intrinsic viscosity (IV)

This was measured in methylene chloride at 20°C using an Ubbelohde viscosimeter.

MFR

This was measured at 300°C with a load of 1 2 kg according to the JIS K-7210 method.

Color matching

An injection-molded plate measuring 3 mm in thickness was molded at a cylinder temperature of 290°C, an injection pressure of 1 000 kg/cm, a cycle time of 45 seconds, and a mold temperature of 100°C. X, Y, and Z values were measured using the ND-1001 DP Colorand color difference meter manufactured by Nihon Denshoku Kogyo K.K. using the transmission method, and yellow index [YI] was measured.

$$YI = 100\,(1\,277\,X - 1\,060\,Z)/Y$$

Optical transmittance

This was measured according to the ASTM D 1003 method using an injection-molded plate for color matching measurement.

Haze

The haze of an injection-molded plate for color matching measurement was measured using an NDH-200 manufactured by Nihon Denshoku Kogyo K.K.

Retention stability

After the resin was retained in the cylinder of an injection molding machine for 15 minutes at a temperature of 320°C, injection molding was carried out at this temperature, the molded plate obtained was measured for MFR and color matching (YI), and the rate of increase in MFR compared to MFR in the initial phase was calculated.

Water resistance

An injection-molded plate for color matching measurement was immersed in water in an autoclave and then maintained at 125°C in an oven for 5 days. Haze was then measured using this test piece.

Practical Example 1

0.44 kilomoles of bisphenol A (Nihon G.E. Plastics K.K.) and 0.46 kilomoles of diphenyl carbonate (manufactured by Enya Co.) were placed in a 250-1 tank-type agitating tank and dissolved at 140°C following nitrogen purging.

Next, the temperature of the mixture was increased to 180°C, and as a catalyst, a solution of tetramethylammonium hydroxide, phenol, and water in a molar ratio of 2.5 : 3 : 20 and a solution of sodium hydroxide, phenol, and water in a molar ratio of 1 : 10 : 60 were mixed and added to a concentration of 0.11 moles of tetramethylammonium hydroxide (2.5×10^{-4} moles/mole of bisphenol A) and 0.00044 moles of sodium hydroxide (1×10^{-6} moles/mole of bisphenol A), and the mixture was agitated for 30 minutes.

After this, as the temperature was increased to 210°C, the pressure was gradually decreased to 200 mmHg, and

after 30 minutes. the temperature was increased to 240°C while simultaneously decreasing the pressure to 15 mmHg, the amount of phenol distilled while temperature and pressure were kept constant was measured. and the tank was returned to atmospheric pressure using nitrogen at the moment when no more phenol was distilled. The time required for the reaction was 1 hour. The intrinsic viscosity [IV] of the reaction products obtained was 0.15 dl/g.

Next. these reaction products were pressurized using a gear pump and sent to a centrifuge-type thin-film evaporator. and the reaction was continued. The temperature and pressure of the thin-film evaporator were controlled at 270°C and 2 mmHg respectively. Using the gear pump, the mixture was sent from the lower portion of the evaporator at a rate of 40 kg/hour into a biaxial horizontal agitation polymerization tank (L/D = 3. agitation vane rotation diameter 220 mm internal volume 80 l) controlled at a temperature of 295°C and a pressure of 0.2 mmHg, and polymerization was carried out with a dwell time of 30 minutes.

Next. with the mixture in a molten state. the polymer was sent using the gear pump into a biaxial extruder (L/D = 17.5. barrel temperature 285°C), an amount of butyl p-toluenesulfonate greater by a molar factor of 2 than the amount of sodium hydroxide and 100 ppm of distilled water with respect to the resin were kneaded, and the mixture was made into strands by passing through a dye and then cut into pellets using a cutter.

The intrinsic viscosity [IV] of the polymer obtained was 0.49 dl/g.

These results are shown in Table 1

Comparison Examples 1-6

Pellets were obtained by the same method as in Practical Example 1. except that instead of the monohydroxy compound used with respect to the nitrogen-containing basic compound in Practical Example 1, the catalysts. amounts of water and addition methods shown in Table 1 were used.

The results are shown in Table 1

Practical Examples 2-6

Pellets were obtained by the same method as in Practical Example 1. except for the [illegible] that the catalysts. types and amounts of monohydroxy compounds. amounts of water. and addition methods shown in Table 1 were used.

The results are shown in Table 1

Practical Example 7

Pellets were obtained by the same method as in Practical Example 1. except for the fact that together with the twofold molar amount of butyl p-toluenesulfonate with respect to sodium hydroxide and the 100 ppm of distilled water with respect to the resin used in Practical Example 1. 300 ppm of tris(2.4-di-t-butylphenyl) phosphite (Mark 2112: manufactured by Adeka Gas) and 300 ppm of 3.4-epoxycyclohexylmethyl 3',4'-epoxycyclohexanecarboxylate (Seloxide 2021P: manufactured by Daicel Chemical Co.) were kneaded in.

The results are shown in Table 1

Comparison Example 7

Pellets were obtained by the same method as in Comparison Example 2. except for the fact that together with the twofold molar amount of butyl p-toluenesulfonate with respect to sodium hydroxide and the 100 ppm of distilled water with respect to the resin used in Comparison Example 2, 300 ppm of tris(2.4-di-t-butylphenyl) phosphite (Mark 2112: manufactured by Adeka Gas) and 300 ppm of 3.4-epoxycyclohexylmethyl 3',4'-epoxycyclohexanecarboxylate (Seloxide 2021P: manufactured by Daicel Chemical Co.) were kneaded in.

The results are shown in Table 1.

Table 1

	Practical Example 1	Practical Example 2	Practical Example 3
Catalyst dispersion			
(a) Alkali compound	NaOH	NaOH	NaOH
(x 10^{-7} moles/BPA)	10	10	10
Monohydroxy compound	Phenol	Phenol	-
(x 10^{-7} moles/BPA)	100	300	-
Water (x 10^{-7} moles/BPA)	600	2000	-
(b) Nitrogen-containing compound	Tetramethylammonium hydroxide	Tetramethylammonium hydroxide	Tetramethylammonium hydroxide
(x 10^{-4} moles/BPA)	2.5	2.5	2.5
Monohydroxy compound	Phenol	Phenol	Phenol
(x 10^{-4} moles/BPA)	3.0	3.0	3.0
Water (x 10^{-4} moles/BPA)	20	20	20
Addition method	Solutions (a) and (b) added after mixing	Solutions (a) and (b) added separately	Solutions (a) and (b) added separately
[B] Acidic compound Amount used (mole factor/ catalyst (a))	butyl p-toluenesulfonate 2.0	butyl p-toluenesulfonate 2.0	butyl p-toluenesulfonate 2.0
[C] Water (ppm)	100	100	100
Initial-stage properties			
[IV] (dl/g)	0.49	0.49	0.49
MFR (g/10 minutes)	10.3	10.3	10.3
YI	1.25	1.32	1.36
Optical transmittance (%)	90.8	90.8	90.8
Haze	0.2	0.2	0.2
Retention stability			
MFR (g/10 minutes)	10.5	10.5	10.5
MFR increase rate (%)	2	2	2
YI	1.33	1.40	1.42
Water-resistance Haze	1.7	1.7	1.8

Table 1 (cont. 1)

	Comparison Example 1	Comparison Example 2	Comparison Example 3
Catalyst dispersion			
(a) Alkali compound	NaOH	NaOH	NaOH
(x 10^{-7} moles/BPA)	10	10	10
Monohydroxy compound	Phenol	-	-
(x 10^{-7} moles/BPA)	300	-	-
Water (x 10^{-7} moles/BPA)	-	-	600
(b) Nitrogen-containing compound	Tetramethylammonium hydroxide	Tetramethylammonium hydroxide	Tetramethylammonium hydroxide
(x 10^{-4} moles/BPA)	2.5	2.5	2.5
Monohydroxy compound	-	-	-
(x 10^{-4} moles/BPA)	-	-	-
Water (x 10^{-4} moles/BPA)	20	20	20
Addition method	Solutions (a) and (b) added separately	Solutions (a) and (b) added separately	Solutions (a) and (b) added after mixing
[B] Acidic compound Amount used (mole factor/ catalyst (a))	butyl p-toluenesulfonate 2.0	butyl p-toluenesulfonate 2.0	butyl p-toluenesulfonate 2.0
[C] Water (ppm)	100	100	100
Initial-stage properties			
[IV] (dl/g)	0.49	0.49	0.49
MFR (g/10 minutes)	10.3	10.3	10.3
YI	1.55	1.83	1.80
Optical transmittance (%)	90.8	90.8	90.8
Haze	0.2	0.2	0.2
Retention stability			
MFR (g/10 minutes)	10.5	10.5	10.5
MFR increase rate (%)	2	2	2
YI	1.64	2.13	2.10
Water-resistance Haze	2.0	2.7	2.6

Table 1 (cont. 2)

	Practical Example 4	Practical Example 5	Practical Example 6
Catalyst dispersion			
(a) Alkali compound	NaOH	NaOH	NaOH
(x 10^{-7} moles/BPA)	5	5	5
Monohydroxy compound	Phenol	Methanol	-
(x 10^{-7} moles/BPA)	100	100	-
Water (x 10^{-7} moles/BPA)	600	-	-
(b) Nitrogen-containing compound	Tetramethylammonium hydroxide	Tetramethylammonium hydroxide	Tetramethylammonium hydroxide
(x 10^{-4} moles/BPA)	2.5	2.5	2.5
Monohydroxy compound	Phenol	Methanol	-
(x 10^{-4} moles/BPA)	3.0	20	-
Water (x 10^{-4} moles/BPA)	20	-	20
Addition method	Solutions (a) and (b) added after mixing	Solutions (a) and (b) added after mixing	Solutions (a) and (b) added after mixing
[B] Acidic compound Amount used (mole factor/ catalyst (a))	butyl p-toluenesulfonate 2.0	butyl p-toluenesulfonate 2.0	butyl p-toluenesulfonate 2.0
[C] Water (ppm)	100	100	100
Initial-stage properties			
[IV] (dl/g)	0.49	0.49	0.49
MFR (g/10 minutes)	10.3	10.3	10.3
YI	1.15	1.35	1.62
Optical transmittance (%)	90.8	90.8	90.8
Haze	0.2	0.2	0.2
Retention stability			
MFR (g/10 minutes)	10.5	10.5	10.5
MFR increase rate (%)	2	2	2
YI	1.23	1.42	1.89
Water-resistance Haze	1.2	1.5	1.8

Table 1 (cont. 3)

	Practical Example 6	Comparison Example 5	Comparison Example 6
Catalyst dispersion			
(a) Alkali compound	NaOH	NaOH	NaOH
(x 10^{-7} moles/BPA)	20	20	100
Monohydroxy compound	Phenol	-	Phenol
(x 10^{-7} moles/BPA)	200	-	1000
Water (x 10^{-7} moles/BPA)	1000	-	-
(b) Nitrogen-containing compound	Tetramethylammonium hydroxide	Tetramethylammonium hydroxide	-
(x 10^{-4} moles/BPA)	2.5	2.5	-
Monohydroxy compound	Phenol	-	-
(x 10^{-4} moles/BPA)	3.0	-	-
Water (x 10^{-4} moles/BPA)	20	20	-
Addition method	Solutions (a) and (b) added after mixing	(a) and (b) added after mixing	Solution (a) added alone
[B] Acidic compound Amount used (mole factor/catalyst (a))	butyl p-toluenesulfonate 2.0	butyl p-toluenesulfonate 2.0	butyl p-toluenesulfonate 2.0
[C] Water (ppm)	100	100	100
Initial-stage properties			
[IV] (dl/g)	0.49	0.49	0.49
MFR (g/10 minutes)	10.3	10.3	10.3
YI	1.43	2.07	2.95
Optical transmittance (%)	90.8	90.7	90.6
Haze	0.2	0.3	0.4
Retention stability			
MFR (g/10 minutes)	10.8	11.1	12.4
MFR increase rate (%)	5	8	20
YI	1.56	2.43	3.43
Water-resistance Haze	2.9	3.9	50

Table 1 (cont. 4)

	Practical Example 7	Comparison Example 7
Catalyst dispersion (a) Alkali compound (x 10^{-7} moles/BPA) Monohydroxy compound (x 10^{-7} moles/BPA) Water (x 10^{-7} moles/BPA) (b) Nitrogen-containing compound (x 10^{-4} moles/BPA) Monohydroxy compound (x 10^{-4} moles/BPA) Water (x 10^{-4} moles/BPA) Addition method	 NaOH 10 Phenol 100 600 Tetramethylammonium hydroxide 2.5 Phenol 3.0 20 Solutions (a) and (b) added after mixing	 NaOH 10 - - - Tetramethylammonium hydroxide 2.5 - - - (a) and (b) added separately
[B] Acidic compound Amount used (mole factor/ catalyst (a))	butyl p-toluenesulfonate 2.0	butyl p-toluenesulfonate 2.0
[C] Water (ppm)	100	100
[D] Additives Phosphorus compound (ppm) Epoxy compound (ppm)	- 300 300	- 300 300
Initial-stage properties [IV] (dl/g) MFR (g/10 minutes) YI Optical transmittance (%) Haze	 0.49 10.3 1.15 90.8 0.2	 0.49 10.3 1.61 90.8 0.3
Retention stability MFR (g/10 minutes) MFR increase rate (%) YI	 10.8 5 1.17	 11.3 10 1.72
Water-resistance Haze	1.5	2.0

Claims

1. A method for manufacturing polycarbonate, characterized in that when an aromatic dihydroxy compound and a carbonic acid diester are subjected to melt polycondensation in the presence of a catalyst including (a) a nitrogen-containing basic compound.

the aforementioned (a) nitrogen-containing basic compound is dissolved or dispersed in a monohydroxy compound or an aqueous solution of a monohydroxy compound to make a catalyst solution. this catalyst solution is added to the melt polycondensation reaction system. and the aromatic dihydroxy compound and the carbonic acid diester are subjected to melt polycondensation.

2. The method for manufacturing polycarbonate of Claim 1. characterized in that a monohydroxy compound produced as a by-product of the polycondensation reaction between the aromatic dihydroxy compound and the carbonic acid diester is used as the monohydroxy compound which forms the catalyst solution.

3. The method for manufacturing polycarbonate of Claim 1. characterized in that the monohydroxy compound which forms the catalyst solution is an aromatic monohydroxy compound.

4. The method for manufacturing polycarbonate of Claim 1. characterized in that the monohydroxy compound which forms the catalyst solution is a phenol

5. The method for manufacturing polycarbonate of Claim 1. characterized in that the (a) nitrogen-containing basic compound is used in the amour of 1×10^{-6} to 1×10^{-1} moles with respect to 1 mole of the aromatic dihydroxy compound.

6. The method for manufacturing polycarbonate of Claim 1. characterized in that the catalyst consists of (a) a nitrogen-containing basic compound and (b) an alkali metal compound and/or alkaline earth metal compound.

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(54) Preparing method of polycarbonate

(57) The present invention provides a method for manufacturing polycarbonate having outstanding color matching, outstanding retention of stability during molding, such as thermal stability and color-matching stability, and outstanding transparency and water resistance.

The method is characterized in that (a) a nitrogen-containing basic compound is used as a catalyst dissolved or dispersed in a monohydroxy compound or an aqueous solution of a monohydroxy compound. This catalyst solution is added to a melt polycondensation reaction system, and an aromatic dihydroxy compound and a carbonic acid diester are subjected to melt polycondensation. It is preferable to use a monohydroxy compound produced as a by-product of a polycondensation reaction between an aromatic dihydroxy compound and a carbonic acid diester as the monohydroxy compound, and it is particularly preferable that the aromatic monohydroxy compound is a phenol.

European Patent Office

EUROPEAN SEARCH REPORT

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EP 95 30 8906

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A D	EP-A-0 360 578 (GE PLASTICS JAPAN LTD) * claims 1-14 * & JP-A-02 175 723 (NIPPON G II PLAST KK) ---	1-6	C08G64/30
D,A	DATABASE WPI Week 9507 Derwent Publications Ltd., London, GB; AN 95-048919 XP002020203 & JP-A-06 329 786 (TEIJIN LTD) , 29 November 1994 * abstract * -----	1-6	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C08G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	4 December 1996	Decocker, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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